

On the energy landscape at the glass transition

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A recent hypothesis claims that the glass transition itself, though it is a very pronounced relaxation peak, is no separate relaxation process at all, but is just the breakdown of the shear modulus due to the weak elastic dipole interaction between all the quasi-independent relaxation centers of the glass. Two derivations are considered, one of them in terms of a breakdown of the shear modulus and the second in terms of a divergence of the shear compliance. Mechanical relaxation data from the literature for vitreous silica, glycerol, polymethylmethacrylate and polystyrene are found to be consistent with the first hypothesis.

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In 1972, Sigi Hunklingers famous experiment¹ demonstrated the two-level nature of the universal low-temperature excitations in glasses.² The experiment gave strong support to the energy landscape concept,³ in which the two-level states are explained in terms of tunneling between adjacent minima of the energy landscape, with a low barrier between them.⁴

If the energy landscape concept is indeed the correct explanation, these two-level states are expected to be a small fraction of a vast number of local relaxation centers in the glass. In this view, the relaxation spectrum of the energy landscape spans a wide range, from the tunneling states at the low-barrier side to the Johari-Goldstein peak⁵ at the high-barrier side. Depending on frequency, this Johari-Goldstein peak is either observed in the glass close to the glass transition temperature T_g or even above T_g in the supercooled liquid.

While the energy landscape concept in itself seems to be reasonably well established, the extent to which it can be represented by an ensemble

U. Buchenau

of independent double-well potentials is a widely debated question. With respect to the tunneling states, this question begins to be answered by experiments in the mK range.⁶ Again, Sigi Hunklinger played a central role in the performance and interpretation of these experiments, approximately thirty years after establishing his scientific reputation with the demonstration of two-level states.¹ According to these new experiments, the concept of isolated tunneling states seems to break down in the mK range. A plausible explanation is the coupling of the tunneling states by the interaction of their elastic dipole moments,⁷ which leads to the formation of coupled pairs of tunneling states.

The present paper deals with the question whether the same elastic dipole interaction provides the key to the unsolved riddle of the glass transition. Here, we assume that this is indeed the case. In particular, we assume that the shear relaxation is due to an ensemble of double-well potentials which are weakly coupled by the interaction of their elastic dipole moments. The ensemble comprises the tunneling states at the low-barrier end as well as the Johari-Goldstein relaxation at the high-barrier end, possibly with rather different atomic jump vectors, but all of them interacting with each other. The reader should be aware that this is only one of many explanations in the literature.^{8,9}

One can treat the elastic-dipole interaction in two different mean-field approaches (i) in terms of the shear modulus (ii) in terms of the shear compliance. Here, equations for both approaches are derived and compared to dynamical mechanical shear data for four glassformers at their respective glass temperatures T_g .

In the shear modulus treatment,¹⁰ one considers a small initial shear deformation ϵ switched on at the time $t = 0$. The initial shear stress $\sigma = G\epsilon$, where G is the infinite frequency shear modulus. The shear stress decay with increasing time is described¹¹ in terms of the rheological function $H(\tau)$

$$G(t) = G - \int_{-\infty}^{\infty} H(\tau)(1 - e^{-t/\tau})d \ln \tau. \quad (1)$$

In the energy landscape concept, relaxation occurs via thermally activated jumps over the barriers V between different energy minima. The corresponding relaxation time τ_V obeys the Arrhenius relation

$$\tau_V = \tau_0 \exp(V/k_B T) \quad (2)$$

with $\tau_0 \approx 10^{-13} s$. Therefore we replace the rheological function $H(\tau)$ by the barrier density function $f(V)$

$$H(\tau_0 e^{V/k_B T}) = H(\tau_V) = G k_B T f(V). \quad (3)$$

On the energy landscape at the glass transition

Inserting this definition into equation (1) for the time dependence of the shear modulus gives

$$G(t) = G \left(1 - \int_0^\infty f(V)(1 - e^{-t/\tau_V})dV \right) \approx G \left(1 - \int_0^{V_t} f(V)dV \right), \quad (4)$$

where V_t is the barrier with $\tau_V = t$.

In order to take the influence of the elastic dipole interaction into account, one assumes a true barrier density $f_0(V)$ of the energy landscape. At the barrier height V_t , the jump between the two minima will tend to occur at the time t , when the shear stress has decreased to $G(t)\epsilon$. Thus the remaining shear stress energy is only a fraction $G(t)^2/G^2$ of the initial one. If we now consider the microscopic situation at the local relaxation center as unchanged, with the same initial shear distortion, then the free energy change by the jumps of the relaxation center remains unchanged. This means that the relaxation center releases the same amount of stress energy. But it reduces a stress energy weakened by $G(t)^2/G^2$, so its effectivity in bringing the shear modulus down to zero is increased by the reverse of this factor.

Therefore the mean-field approach for the shear modulus reads

$$f_0(V) \equiv f(V) \left[1 - \int_0^V f(v)dv \right]^2. \quad (5)$$

In a physical picture, the enhancement of $f_0(V)$ is due to induced jumps of lower-barrier relaxation centers in the neighborhood of the given relaxation center with barrier V , which occur quasi-instantaneously after its jump.

The equation (5) has the back-transformation¹⁰

$$f(V) = \frac{f_0(V)}{\left[1 - 3 \int_0^V f_0(v)dv \right]^{2/3}}. \quad (6)$$

In the shear modulus approach, the breakdown of the shear rigidity occurs when the integral of $f_0(V)$ over V reaches 1/3. The corresponding barrier is called Maxwell barrier, because it determines the Maxwell time τ_M (the shear stress relaxation time) through the Arrhenius relation, eq. (2). It is given by the 1/3-rule derived in ref.¹⁰

$$\int_0^{V_M} f_0(V)dV = \frac{1}{3}. \quad (7)$$

The breakdown occurs in a rather dramatic way, because the relaxing entities at the critical Maxwell barrier value receive a strong enhancement,

U. Buchenau

to such an extent that one is tempted to assume a separate α -process which has nothing to do with the secondary glass relaxations. In fact, this more or less unconscious assumption underlies most of the present attempts to understand the glass transition.⁸ The above treatment shows such an assumption to be unnecessary; what one sees at the glass transition are simple Arrhenius relaxations of no particularly large number density $f_0(V)$, blown up to impressive size in $f(V)$ by the small denominator of eq. (6).

The shear modulus approach can be tested by plotting the product $G''G'^2$ of experimental dynamical shear data as a function of frequency or temperature. In fact, the true barrier density $f_0(V)$ can be calculated approximately from the equation

$$V_M f_0(k_B T \ln \frac{1}{\omega \tau_0}) \approx \frac{2}{\pi} \frac{G'' G'^2}{G^3} \ln \frac{\tau_M}{\tau_0}, \quad (8)$$

where G is again the infinite frequency shear modulus.

One can build the analogue of the shear modulus approach, starting from the shear compliance. In the shear compliance treatment, one considers a small initial shear stress σ switched on at the time $t = 0$. The initial shear distortion $\epsilon = J\sigma$, where $J = 1/G$ is the infinite frequency shear compliance. The shear distortion increase with increasing time is described¹¹ in terms of the rheological function $L(\tau)$

$$J(t) = \frac{1}{G} + \int_{-\infty}^{\infty} L(\tau)(1 - e^{-t/\tau}) d \ln \tau + \frac{t}{\eta_0}, \quad (9)$$

where η is the viscosity. In the following, we omit this viscosity term, because we are only interested in the breakdown of the shear rigidity.

In the energy landscape concept, we replace the rheological function $L(\tau)$ by another barrier density function $l(V)$ defined by

$$L(\tau_0 e^{V/k_B T}) = L(\tau_V) = \frac{k_B T l(V)}{G}. \quad (10)$$

Inserting this definition into equation (9) for the time dependence of the shear compliance gives

$$J(t) = \frac{1}{G} \left[1 + \int_0^{\infty} l(V)(1 - e^{-t/\tau_V}) dV \right] \approx \frac{1}{G} \left[1 + \int_0^{V_t} l(V) dV \right]. \quad (11)$$

where again V_t is the barrier with $\tau_V = t$.

Again, the influence of the elastic dipole interaction is taken into account assuming a true barrier density $l_0(V)$ of the energy landscape. But now, the situation at the barrier height V_t for the time t is different. The shear

On the energy landscape at the glass transition

stress is still the initial one, but the shear distortion has increased by $J(t)G$. Therefore the free energy change by the jumps of the relaxation center is increased by $J(t)^2 G^2$.

Thus the mean-field approach for the shear compliance reads

$$l_0(V) \equiv \frac{l(V)}{\left[1 + \int_0^V l(v)dv\right]^2}. \quad (12)$$

Its back-transformation is

$$l(V) = \frac{l_0(V)}{\left[1 - \int_0^V l_0(v)dv\right]^2}. \quad (13)$$

We see that the results for the shear compliance approach (ii) differ markedly from the shear modulus approach (i) proposed earlier.¹⁰ The Maxwell barrier is now given by the divergence of the compliance

$$\int_0^{V_M} l_0(V)dV = 1. \quad (14)$$

Again, the relaxing entities at the critical Maxwell barrier value receive a strong enhancement. The shear compliance approach can be tested by plotting the ratio J''/J'^2 of experimental dynamical shear data as a function of frequency or temperature. The true barrier density $l_0(V)$ can be calculated approximately from the equation

$$V_M l_0(k_B T \ln \frac{1}{\omega \tau_0}) \approx \frac{2}{\pi} J'' J / J'^2 \ln \frac{\tau_M}{\tau_0}. \quad (15)$$

Since the influence of the viscosity was neglected, this equation is only expected to hold down to the frequency with $\omega \tau_M = 10$, at least for non-polymeric glass formers. This is a drawback of the compliance approach. If one tries to include the viscosity, the equations get complicated and rather difficult to handle.

In any case, one is now able to compare dynamical mechanical shear data from experiment to the two theoretical approaches. Fig. 1 begins with the shear modulus approach, showing $G''G'^2$ -values from measurements at the glass transition. The comparison is done for the four glass formers SiO_2 , glycerol, polystyrene and polymethylmethacrylate. Also included is the simplest theoretical case, with $f_0(V) = constant = 1/3V_M$, the so-called *generic case*. The figure is scaled in such a way that this generic case is 1. The scaling requires the knowledge of the Maxwell time τ_M . For silica and glycerol, the classical Maxwell relation $\tau_M = \eta/G$ was used. For the two

U. Buchenau

polymers, τ_M was taken from the condition $\omega_{max}\tau_M = 1$, where ω_{max} was the maximum of the peak in G'' . In order to cover five decades in such a mechanical measurement, one usually needs to do measurements at several temperatures around T_g and use the time-temperature scaling to obtain the full curve.

The scaling $G''G'/G^3$ also requires the knowledge of the infinite frequency shear modulus G . Therefore one needs not only a measurement of G' and G'' , but also a Brillouin measurement of the transverse sound wave velocity v_t at T_g , to determine G via $G = \rho v_t^2$, where ρ is the density at T_g . Table I summarizes the T_g and G values of the four glass formers, together with the relevant references. The glass temperature for glycerol is somewhat higher than the usual value, because the master curves for G' and G'' were given¹⁷ for this temperature.

Table I: Glass transition data.

substance	SiO ₂	glycerol	polystyrene	polymethylmethacrylate
T_g (K)	1449	192.5	363	383
$G(T_g)$ (GPa)	33.8	4.3	1.5	1.86
$\eta(T_g)$ (GPa s)	2512	10		
τ_M (s)	74.3	2.3	100	100
ref. G	¹²	¹³	¹⁴	¹⁵
ref. G', G''	¹⁶	¹⁷	¹⁸	¹⁹
m	20	53	138	145

In Fig. 1, all four experimental curves show a cutoff at $\omega\tau_M = 1$. If one looks closely, one observes that this experimental cutoff is slightly broader than in the theoretical calculation for the generic case, where a sharp cutoff of $f_0(V)$ at V_M was assumed. The two polymers lie decidedly lower than the generic case, the two other cases lie higher.

The corresponding comparison to the compliance approach in Fig. 2 suffers from the fact that for silica and glycerol, it is only meaningful above $\omega\tau_M = 10$, because of the neglected viscosity. Again, silica shows the strongest rise towards the value $\omega\tau_M = 1$, PMMA the weakest.

But even for the two polymers, which have such a high viscosity that it can be indeed neglected, the compliance approach does not work well; there remains a pronounced peak in the near neighbourhood of $\omega\tau_M = 1$, much more pronounced than in the shear modulus approach of Fig. 1. Therefore we conclude that the shear modulus approach is the better description.

This is not unexpected: The shear modulus approach corresponds to a generalized Maxwell model, with an infinite number of parallel Maxwell

On the energy landscape at the glass transition

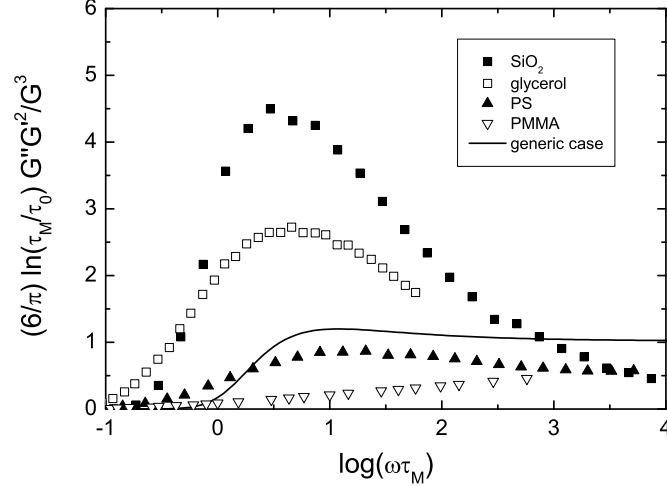


Fig. 1. Comparison of data measured at the glass transition of SiO_2 , glycerol, polystyrene (PS) and polymethylmethacrylate (PMMA) to the generic case $f_0(V) = 1/3V_M$ in the shear modulus approach.

elements, while the shear compliance approach corresponds to an infinite number of Voigt elements in series.¹¹ The description of an ensemble of localized relaxation centers in a three-dimensional viscoelastic continuum in terms of parallel elements is probably more suitable.

Further support for this conclusion is supplied by the obvious connection between the values of the fragility m in Table I (taken from ref.²⁰) and the values of $V_M f_0(V_M)$ extrapolated from Fig. 1. The fragility $m = \partial \log \eta / \partial (T_g/T)$ is defined in terms of the steep rise of the viscosity η towards the glass temperature T_g with decreasing temperature in the supercooled liquid. Silica has the lowest fragility of all known glass formers, while the two polymers belong to the very high fragility end of the scale. A high fragility means a strong decrease of the Maxwell barrier V_M with increasing temperature. Fig. 1 indicates that a high m seems to be related to a low $V_M f_0(V_M)$, and viceversa.

From the 1/3-rule, eq. (7), such a behaviour is expected: If $f_0(V)$ tends to increase with increasing temperature, a low value of $f_0(V_M)$ means a fast decrease of V_M with increasing temperature. Thus one gets at least a qualitative understanding of the old fragility riddle:⁸ With increasing temperature, more and more minima of the energy landscape get populated. This leads to an increase of $f_0(V)$, which in turn leads to a decrease of V_M . This decrease is more dramatic for a low value of $V_M f_0(V_M)$ than for a high one.

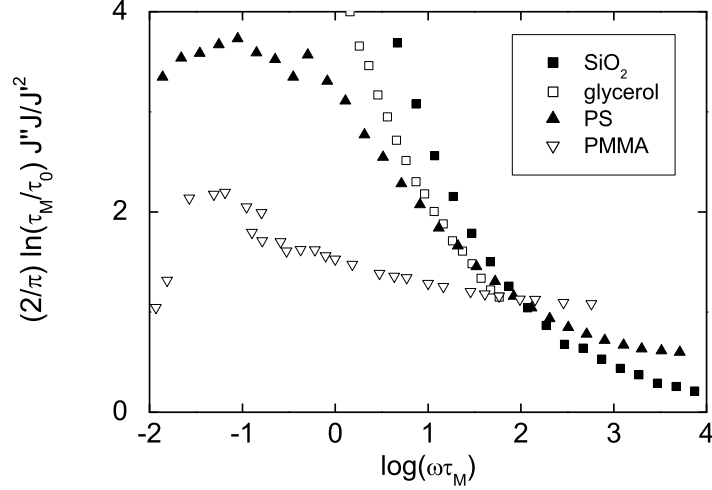


Fig. 2. Comparison of data measured at the glass transition of SiO_2 , glycerol, polystyrene (PS) and polymethylmethacrylate (PMMA) in the shear compliance approach.

Of course, Fig. 1 does not prove the shear modulus description of the glass transition¹⁰ beyond any possible doubt. But the plot of Fig. 1 is a new, quantitative and probably meaningful way to study the relation between the primary relaxation (the shear stress relaxation to the value zero) and the secondary relaxations at higher frequencies.

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On the energy landscape at the glass transition

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